

Observation of Electrically Tunable van der Waals Interaction in Graphene-Molecule Complex

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van der Waals (vdW) interaction plays a fundamental role in the surface-molecules related phenomena. Tuning of the correlated charge fluctuation in the vdW complex is a plausible way to modulate the molecules interaction at the atomic surface. We report vdW interaction tunability of the graphene-CO₂ complex by combining the first principle calculations with the vdW exchange correlation density functionals and the time evaluation measurements of CO₂ molecules adsorption/desorption on graphene under an external electric field. The field-dependent charge transfer within the complex unveils the controllable tuning of CO₂ from acceptor to donor. Meanwhile the configuration of the adsorbed molecule - the equilibrium distance from graphene and O-C-O bonding angle - is modified accordingly. The range of electrical tunability is a unique feature for each type of molecules.

van der Waals (vdW) interaction plays an important role in the surface-related physics and chemistry [1]. It is the decisive factor in the molecular physisorption on a surface [2, 3], adhesion between micro-machined surfaces in the micro- and nano-mechanical devices [4], friction in tribology discipline [5], and the characteristics in the vdW heterostructures [6, 7]. At present, surface modification, i.e. tailoring or replacing the original materials, is a commonly employed method to selectively create specific vdW complexes for their favorable properties [8, 9].

The London dispersion forces involved in a vdW complex of molecules adsorbed on a surface is electro-dynamically correlated to the charge transfer inside the complex. This raises the possibility of tuning such vdW interaction electrically, e.g. by applying external electric field, which offers an easy access to the desired features while keeping the original materials untouched [10–12]. However, we are not aware of any experimental reports on vdW interaction showing the electrical tunability. The difficulty of characterizing the vdW complex impedes the direct observation. In this report, we demonstrate the electrical tunability of the vdW interaction for graphene-molecule complexes with first principle calculations combined with the experimental study of the electrically controlled charge transfer for the graphene-CO₂ vdW complex. As a low-noise Dirac fermion material, graphene is strongly modulated by the vdW interactions with physisorbed molecules upon its transport properties; the inaccessible interaction is therefore transferred into the easily measurable electric signal [13, 14]. The transport measurements verify the tunability of vdW interaction between graphene and CO₂ molecules from the varied charge transfer from molecules to graphene under external fields.

First, the first principle calculations are utilized to understand the interaction between graphene and a CO₂ molecule adsorbed on it [15]. The nonlocal dispersion

relationship associated with the molecular adsorption on graphene is described by using van der Waals density functionals reported by Dion [16, 17]. The potential energy surface scans show the adsorbed CO₂ molecule lie most stably in the direction perpendicular to the carbon-carbon bond of the graphene hexagon, sitting at an equilibrium distance of 3.2 Å with an energy of 170 meV. The low adsorption energy reflects a weak interaction between the CO₂ molecule and the graphene and its physisorption nature. This is also revealed by the density of states (DOS) calculations [18–20] as the electronic states of CO₂ are superimposed on to these of the graphene (Fig. 1A). The weak interaction of the highest occupied molecular orbital (HOMO) of CO₂ (the peak showed at -9.31159 eV in Fig. 1A) with the graphene states results in a small bonding-antibonding splitting of 11.92 meV (Fig. 1B). The 3-dimensional plots of the wavefunctions visually elucidate these abstract features. Figure 1C depicts the bonding wavefunction at -9.60327 eV showing a weak graphene-CO₂ orbitals overlap while a repulsion is noted in its antibonding wavefunction at -9.59135 eV as showed in Fig. 1D. Furthermore, these interacting CO₂ states still locate energetically far below the Fermi level clarifies the weak charge transfer within the graphene-CO₂ complex. Consequently, the van der Waals interaction plays a dominant factor in the graphene-CO₂ complex interaction

Now, we unveil the electrical tunability of the graphene-CO₂ molecule vdW complex by carrying out first principles calculation with Mulliken population analysis [22]. The vdW complex is investigated under external electric field, E_t , applied perpendicularly to graphene. In practice, the electric field is usually introduced to graphene surface by applying voltage, V_T to the substrate. A finite element simulation is first employed to estimate the strength of electric field generated with the application of V_T , which shows E_t of -0.15 V/Å (0.15

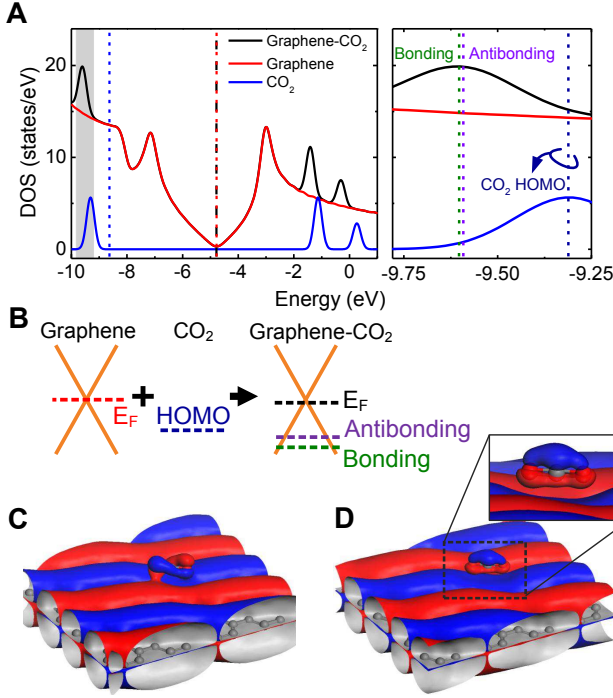


FIG. 1. Density of States and wavefunctions of a graphene- CO_2 complex. (A) DOS plots of graphene- CO_2 complex, graphene, and CO_2 molecule. Vertical dash-lines locate their Fermi levels at -4.7840 eV, -4.7788 eV, and -8.6309 eV, respectively. The right panel is the zoomed-in details of the grey region. (Gaussian broadening energy in DOS plots: 0.2 eV) (B) Schematic of the bonding-antibonding splitting in graphene- CO_2 complex. (C) and (D) visualize bonding (-9.60327 eV) and anti-Bonding (-9.59135 eV) Gamma point wavefunctions of graphene- CO_2 complex, respectively. Blue and red colors denote the positive and negative iso-surface (Iso-value: 0.005).

$\text{V}/\text{\AA}$) is achieved on the graphene surface for V_T of 40 V (-40 V) (Fig. 2A). The charge transfer from the CO_2 molecule to graphene, ΔQ , is calculated with varying E_t . Figure 2B plots the calculated charge transfer as a function of electric field. Without applying a tuning field, CO_2 molecule acts as a weak acceptor to graphene, receiving 0.003e charge. The varied ΔQ is noted as E_t is introduced, disclosing the nature of tunable charge transfer in the vdW complex. In particular, the CO_2 molecules switch their role to donor in the field of 0.15 $\text{V}/\text{\AA}$ (Fig. 2B). The switched polarity of the graphene- CO_2 molecule complex system under the electric fields is also exhibited as a change in the electric dipole moments (figs. S10 and S11).

The predicted tunable charge transfer in the vdW complex, if any, should be measured as varied doping concentration in graphene under the tuning electric fields. In order to prove the above theoretical findings, we measure the variations of doping concentrations, n_d , in graphene exposed to CO_2 molecules under various values of V_T .

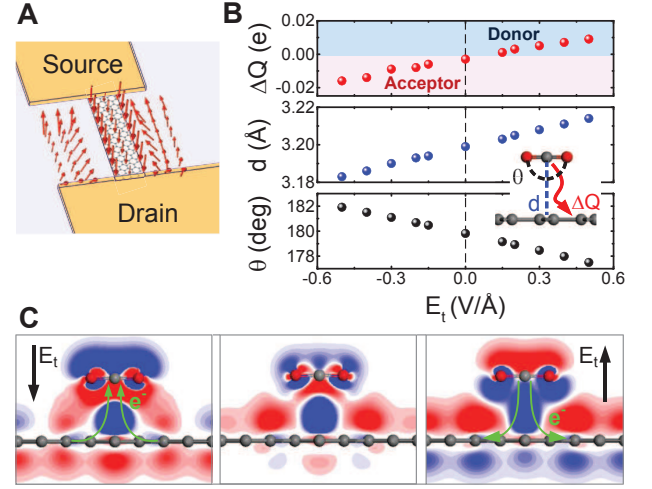


FIG. 2. Electrical tuning of van der Waals bonding of CO_2 molecule to graphene. (A) Finite element simulation showing the direction of electric field at the surface of 2 Å above graphene with 40 V applied back gate voltage. (B) First principle calculations of charge transfer ΔQ , bonding distance d and bending angle θ of the adsorbed CO_2 molecule on graphene at various tuning electric fields. Inset illustrates an adsorbed molecule. (C) Charge density distributions in the cut planes across the CO_2 at varied electrical fields (tuning voltages). From left to right: -0.15 $\text{V}/\text{\AA}$ (40 V), 0 $\text{V}/\text{\AA}$ (0 V), and 0.15 $\text{V}/\text{\AA}$ (-40 V). Blue color denotes electron density enrichment and red color shows depletion for the iso-values of ± 0.0001 electrons/ \AA^3 .

Figure 3A illustrates the schematic of the device and measurement configuration. The gate modulation measurements are carried out along with the time, from which the doping concentrations are extracted (Fig. 3B). Thermal annealing at $\sim 10^{-4}$ Pa is employed *in situ* to regenerate graphene by cleansing the adsorbates before each measurement [14]. For V_T ranging from 0 V to 40 V, positive increases in the doping concentration n_d are observed, which indicate the adsorbed CO_2 molecules act as acceptor. Interestingly, for V_T of -40 V, the negative n_d is measured, signifying the CO_2 molecules act as donor. These results strongly substantiate the prediction of the first principle calculations.

We can extract the value of the average charge transfer $\overline{\Delta Q}$ from Fig. 3B with a simple dynamic model [24]. Then, doping concentration is expressed as $n_d(t) = N(t)\overline{\Delta Q}$, where $N(t)$ represents the temporal density of CO_2 molecules adsorbed on graphene and is described

$$N(t) = \frac{n_0 p_a}{p_d} (1 - e^{-p_d t}) + N_0, \quad (1)$$

where n_0 is the density of the molecules in the gas phase (remains constant after gas injection is stopped), N_0 is the initial adsorption density on graphene, p_a and p_d are the adsorption and desorption rates, respectively. By fitting Eq. (1) to the measured temporal change in the

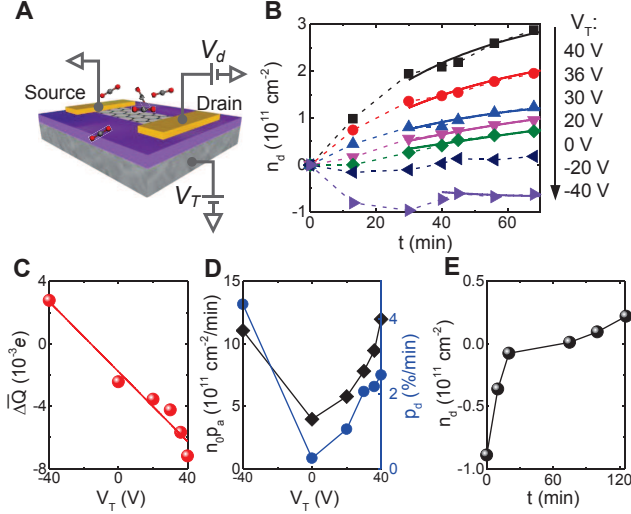


FIG. 3. Measurements of CO_2 adsorptions at varied tuning voltages V_T . (A) Schematic of the measurement configuration. Tuning voltage, V_T , is applied at substrate. (B) Doping concentration at various tuning voltages, V_T , from 40 V to -40 V. The positive/negative sign of n_d denotes hole/electron. The solid lines are the fits to Eq. (1). (C) and (D) plot the values of averaged change transfer ΔQ , adsorption rate $n_0 p_a$ and desorption rate p_d , respectively. Solid line in (C) is the linear fit. (E) Change of doping concentration after tuning voltage switched from -40 V to 40 V.

adsorption density, the values of ΔQ are obtained for different V_T . Fig. 3C clearly manifests the charge transfer tuned via applied external fields, showing a good agreement with the first principles calculation prediction. Besides, the adsorption and desorption rates are also extracted from the data fittings (Fig. 3D). The adsorption rate enhanced by the increased magnitude V_T , accelerates the adsorption process due to the polarizability of the CO_2 molecules. Hence, the similar adsorption rates are read for V_T of -40 V and 40 V. In contrast, the desorption rate at V_T of -40 V is approximately twice as high as compared with that for V_T of 40 V, as a result of a weaker vdW interaction between CO_2 molecule and graphene at -40 V, reflecting a longer bonding distance and lower charge transfer (Fig. 2B).

It is noted that the application of constant voltage V_T is shortly interrupted for an interval of ~ 0.5 min at each individual data point in a series of temporal measurement. During the interval, V_T is swept from -40 V to 40 V in order to obtain gate modulation curves for n_d extraction. Under these circumstances, the charge transfer from those previously adsorbed molecules is probably altered; and molecules freshly adsorbed during the sweeping exhibit varied charge transfer different from that adsorbed under constant V_T . Here we carry out a measurement at an extreme condition to clarify the interruption of constant V_T only slightly affecting the analysis of n_d at constant V_T . Graphene is firstly kept at $V_T = -40$ V for

TABLE I. Electrical tunability of the Charge transfer in various graphene-molecule complexes. Negative and Positive signs indicate the role of molecules as acceptor and donor, respectively.

Molecule	ΔQ (e)		
	-0.15 V/Å	0 V/Å	0.15 V/Å
CO_2	-0.006	-0.003	+0.001
C_6H_6	0.009	+0.019	+0.029
CO	-0.003	+0.001	+0.004
NH_3	+0.015	+0.018	+0.022
O_2	-0.242	-0.208	-0.174

2 hours; a n_d of $-0.89 \times 10^{11} \text{ cm}^{-2}$ is measured (Fig. 3E). Then V_T is suddenly switched to 40 V; the positive shift of n_d with a relatively slow rate of $-0.4 \times 10^{10} \text{ cm}^{-2}/\text{min}$ is observed. Hence, the short interruption of constant V_T has only insignificant impact on the extraction of n_d for V_T . It also suggests that the electrical tuning plays a part during the formation of physisorption or the vdW complex; that is to say once the complex formed, it is stable to some extent.

In order to clarify the tunable charge transfer, we visualize the two-dimensional charge density difference distributions in the graphene- CO_2 complex in Fig. 2C [23] under the tuning field of -0.15 V/Å (left), zero (center), and 0.15 V/Å (right). Here, the charge density difference of CO_2 adsorption is defined by $\rho_{Ad} = \rho_{\text{CO}_2+\text{Gra}} - \rho_{\text{CO}_2} - \rho_{\text{Gra}}$, where $\rho_{\text{CO}_2+\text{Gra}}$, ρ_{Gra} , and ρ_{CO_2} are the charge densities of the graphene with adsorbed CO_2 , the pristine graphene and an isolated CO_2 molecule, respectively. The tunability of the charge transfer can be understood by applying Lorentz force. For a zero tuning field, the vdW interaction governs the charge transfer between CO_2 and graphene, which can be seen from the induced dipole structure between them. As the tuning field is switched on, a strong electrostatic force induces a comparable order of charge redistribution inside the vdW complex; that is to say, the charge transfer is tuned electrically. Under positive (negative) tuning fields, more electrons are taken from (given to) the CO_2 molecule (movie S1). The reversed dipole distribution are clearly seen for the negative and positive tuning fields (left and right of Fig. 2C). This is associated with the change in other parameters for the graphene- CO_2 vdW interactions. Particularly, the vdW bonding distance, d , is changed from 3.199 Å at the natural state to 3.203 Å (3.194 Å) for E_T of 0.15 V/Å (-0.15 V/Å). The bonding angle between carbon and oxygen atoms also varies accordingly (Fig. 2B).

We extend the present theoretical investigation to other graphene-molecules complexes. In Table I, we compare the their charge transfer ΔQ calculated for various vdW complexes at the negative, zero, and positive tuning

fields [14, 25, 26]. The results indicate that the individual complexes show different tunabilities. It should also be noted that such a unique tunability does not depend on the initial conditions of graphene. Thus, additional to the conductivity change of graphene stemmed from the molecular adsorptions - a commonly employed gas sensing mechanism, the observation of the doping tunability may provide a new approach to the gas molecule detection.

With the complex of graphene and its phsisorbed CO₂ molecules, we have discovered the tunability of the vdW interaction at external electric fields. The charge transfer in a vdW complex is tuned electrically, thereby changing other parameters of interaction thereupon. Our results entice us to attempt the possibility of recognizing the type of molecules with graphene from the unique tunable change transfer between them.

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